MICROSCOPY WITH ELECTRONS – I

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October 25, 2022

OUTLINE OF THE LECTURES

I – October 25, 2022

- History of (electron) microscopy
- Properties of the electron
- Focusing and Imaging
- Electron-material interaction
- SEM

II – December 6, 2022

- SEM / TEM techniques
  - EDS
- TEM
- TEM usages
- Micro-probe

HISTORY - OPTICAL MICROSCOPES

Microscope: examining a parameter of the sample as a function of space.

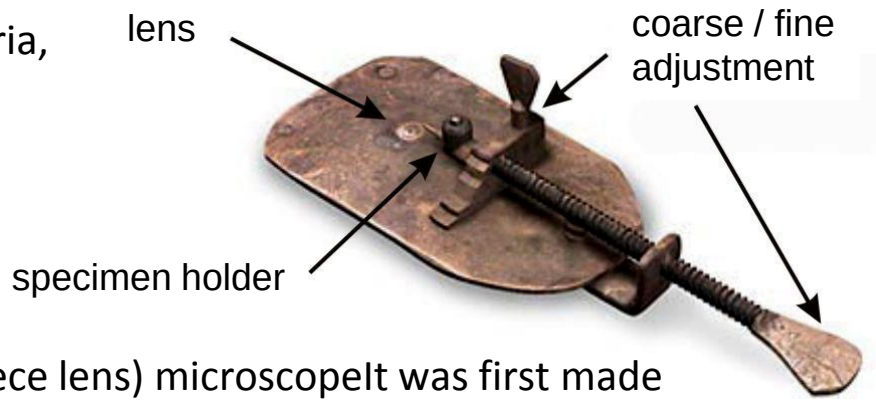
The result is the microscope image. There are many kinds of microscopes and many imaging methods.

Optical microscopy
It works with visible light. Science used such a microscope for the first time.

Antonie van **Leeuwenhoek** (1632-1723, Netherlands)He produced his one-lens microscope with the highest magnification (~ 300) of his age.

He applied it with scientific requirements.

He discovered single cells, bacteria, red blood cells, and so on.



Complex (multi-lens, lens, eyepiece lens) microscopeIt was first made in the Netherlands in the 1600s

HISTORY - OPTICAL MICROSCOPES

In the 18th and 19th centuries, the creation of a microscope (magnifiers, binoculars) became a thriving industry.

In 1762, **Euler** wrote a dissertation on the acromats.

In 1845, another breakthrough came in microscopy: the first arc lamps appeared.

In 1847 **Carl Zeiss** presented his first microscope.

Later, the Zeiss factory in Jena produced lenses and condensers which was developed by **Ernst Abbe**.

One of the directions of development is the correction of lens defects.

In 1872, Abbe's imaging theory appears.

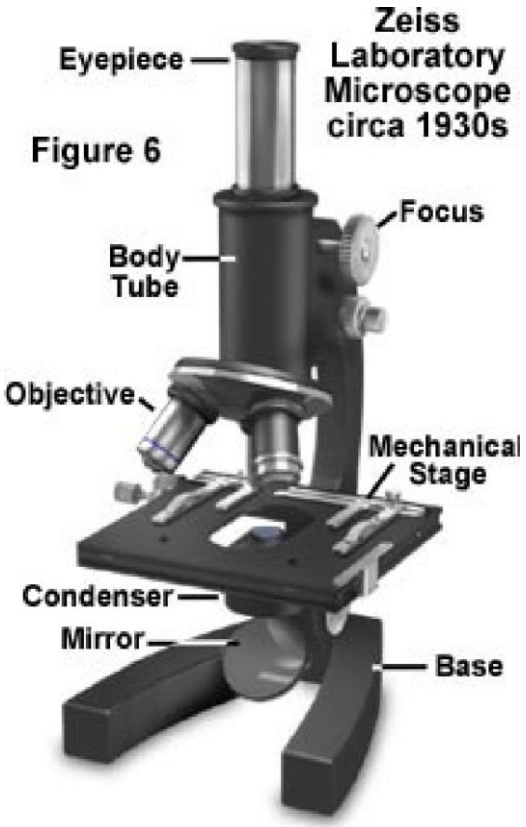


Figure 6

ABBE'S IMAGING THEORY

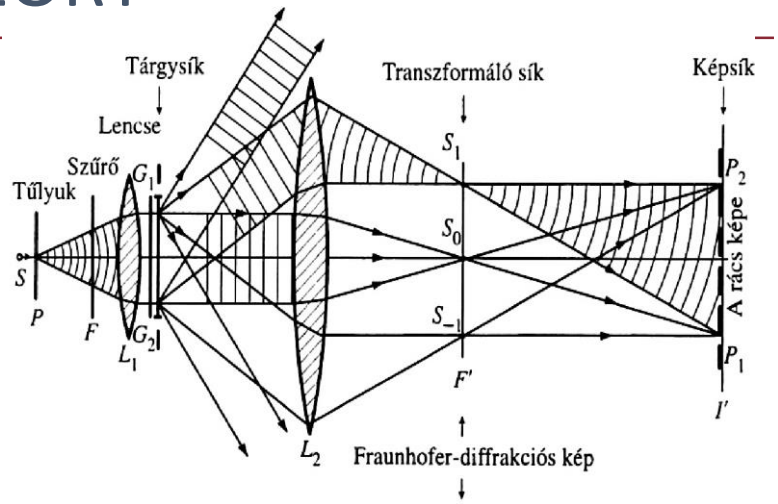
Abbe described the operation of the lens based on the wave optics.

Amplitude object

Grid-like object -> deflection orders.

These parallel beams are merged into dots in the focal plane.

Same as Fraunhofer diffraction pattern.



The individual points correspond to the different diffraction patterns, their intensity is the Fourier components of the Fourier transform of the object intensity function.

Thus, the lens produces the *F [f (x, y)]* Fourier transform of the function *f (x, y)* describing the permeability of the object in the focal plane.

The higher orders are more away from the optical axis.

These correspond to the increasing spatial frequencies (higher frequency Fourier components).

They also have phases!

If the object descriptor function is not periodic, then the Fourier transform is created, but not discrete points, but continuously changing intensity in the focal plane.

ABBE'S IMAGING THEORY

Phase object case

The object hardly changes the amplitude, but some parts change the phase of the passing light.

In this case, the object details are not visible on the microscope, as our eyes (and our detectors) are not sensitive for the phase change.

$T(x, y) = e^{i\Phi(x,y)}$ the amplitude considered to be 1,

$\Phi(x, y) \sim n(x,y)\, t$ ***n*** - refractive index of the object's material, ***t*** - thickness,

$T(x, y) \approx 1 + i\,\Phi(x, y)$ series expansion,

$\mathfrak{I}(T(x, y)) \approx \mathfrak{I}(1) + i\,\mathfrak{I}(\Phi(x, y))$ Fourier transform

The first tag is the maximum at the center of the optical axis.

Its extent is practically the maximum intensity concentrated near to the optical axis.

The second tag is generally a wide range of beams of phase $\pi/2$ (due to the multiplier i) is different from the phase of the central beam.

THE RESOLUTION OF LENSES

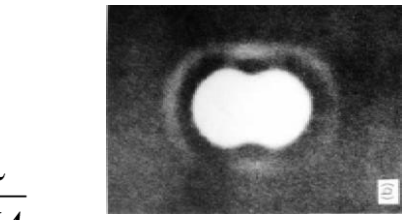
One of the most important parameters of the lens.

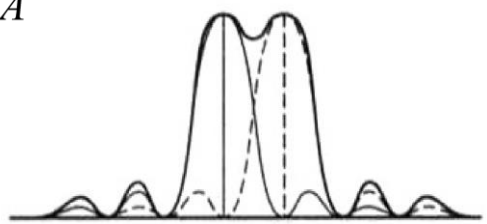
The resolution is the smallest distance between two points of the object that is large enough to give distinct points on the image.

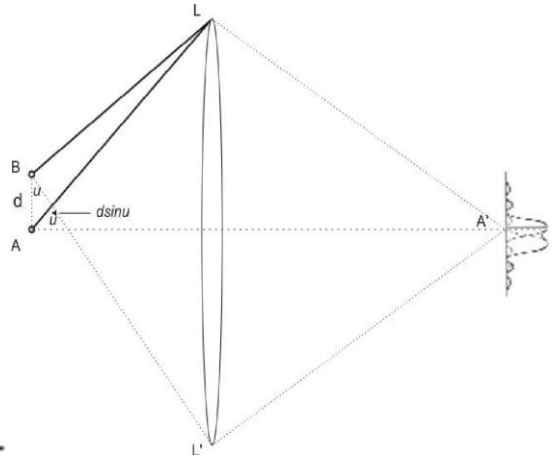
Resolution is somewhat subjective, so agreements (similar) define it.

Rayleigh criterion:
two point sources are regarded as just resolved when the principal diffraction maximum of one image coincides with the first minimum of the other.

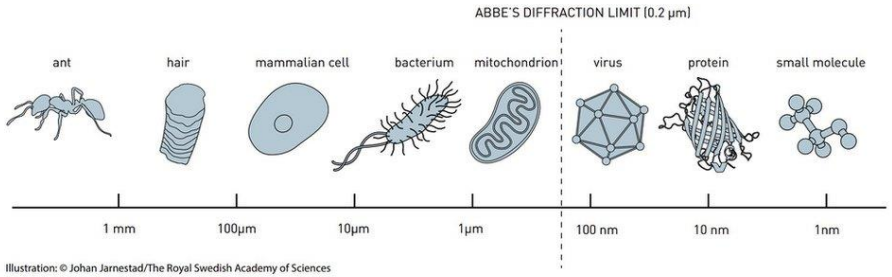
$$d = 0{,}61\frac{\lambda}{n\sin u} = 0{,}61\frac{\lambda}{NA}$$

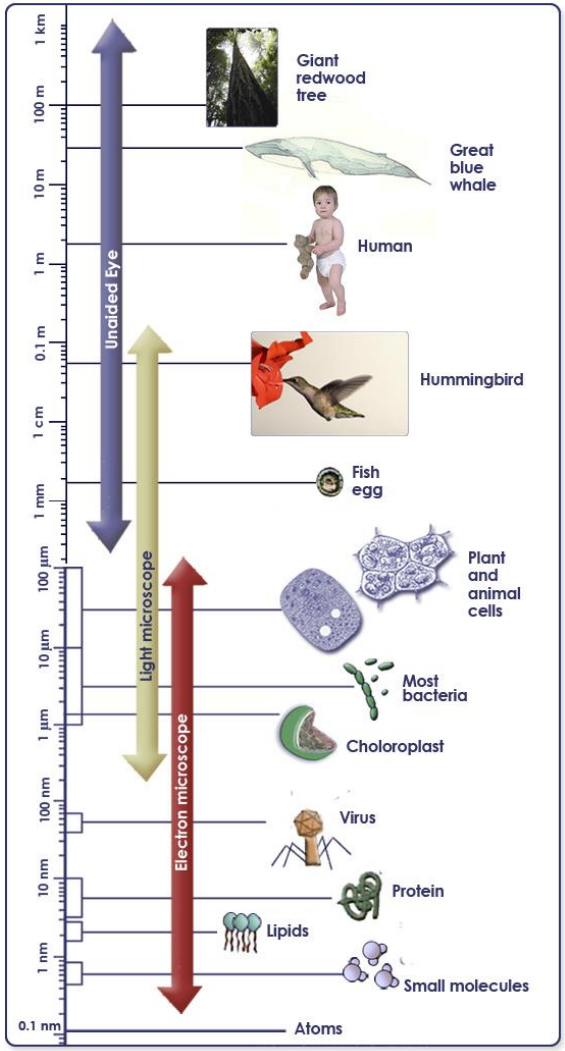






WHAT RESOLUTION DO WE NEED?

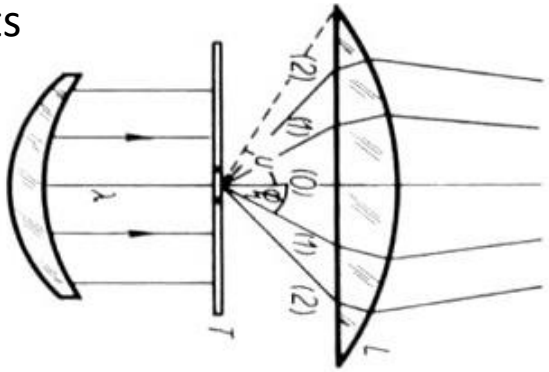




ABBE CONDITION

Let points A and B at distance d, on which deflection occurs.
The zero-order maximum will be on the axis.
And for the higher deflection maxima one gets

$$\sin\alpha = \frac{k\lambda}{d} \qquad ,k = 0,\pm1,\pm2,\ldots$$



According to Abbe, at least two deflection regimes must be involved in the generation of the image to separate the two points.

If k = 1 and k = -1 deflections also pass through the lens:

$$d = \frac{\lambda}{\sin u}$$

If the refractive index is n of material between the object and the lens, instead of wavelength λ λ/n should be written.

$$d = \frac{\lambda}{n\sin u} = \frac{\lambda}{NA}$$

ABBE CONDITION

Satisfying that only the zero-order maximum with the +1 (or -1) first-order maximum pass through the lens and using oblique illumination, the resolution decrease to the half:

$$d = \frac{1}{2}\frac{\lambda}{n \sin u} = 0{,}5\frac{\lambda}{n \sin u}$$

The Rayleigh and the Abbe condition provides very similar results.

Usually $n \sim 1$ and $max(\sin u) = 1$ so the maximum theoretical resolution of the microscope is $\sim \lambda/2$.

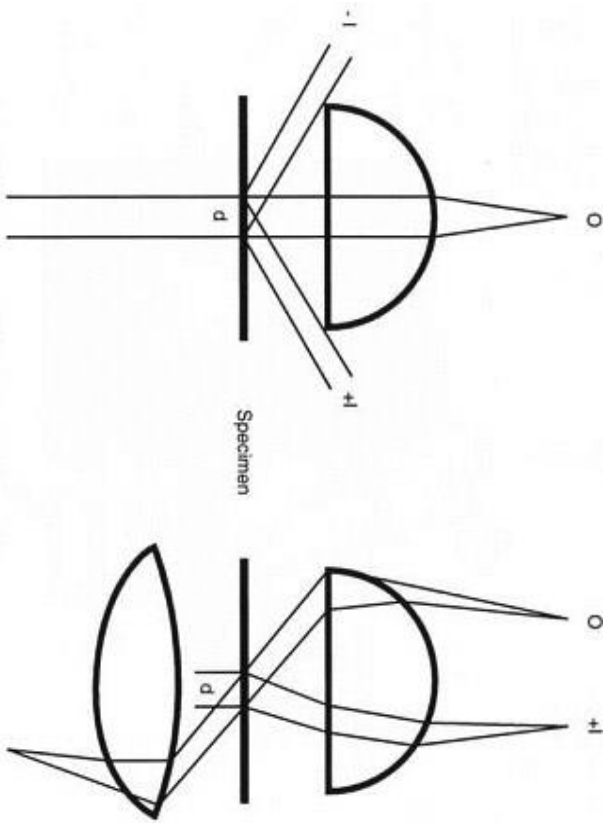
Eg. if $\lambda = 550\ nm$ (green, the max. sensitivity of the eye) then

$$d_{max} \sim 250\ nm.$$

This can be reduced a bit for

$$d_{max} \sim 130\ nm,$$

but it is hard to reach.

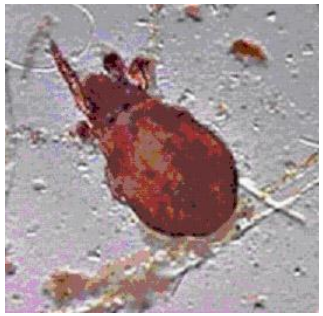


MAGNIFICATION

Magnification

$$M = \frac{I}{O}$$

The maximum magnification is the value that magnifies the smallest distance as much as the value of the eye's maximum resolution (~ $0.15\ mm$).



For optical microscope:

$$M\,\frac{\lambda}{2NA} = 0{,}15\,mm$$

$$M = \frac{2NA \cdot 0{,}15\,mm}{\lambda}$$

With the appropriate values for visual observation for $\lambda = 550\ nm$ the maximum useful magnification is ~ $500 \cdot NA$.

Of course, it is possible to apply larger magnifications, but it not gives newer details about the object.

This is called blank magnification. In this case, the image loses its sharpness (will be pixelized) and the brightness is also reduced.

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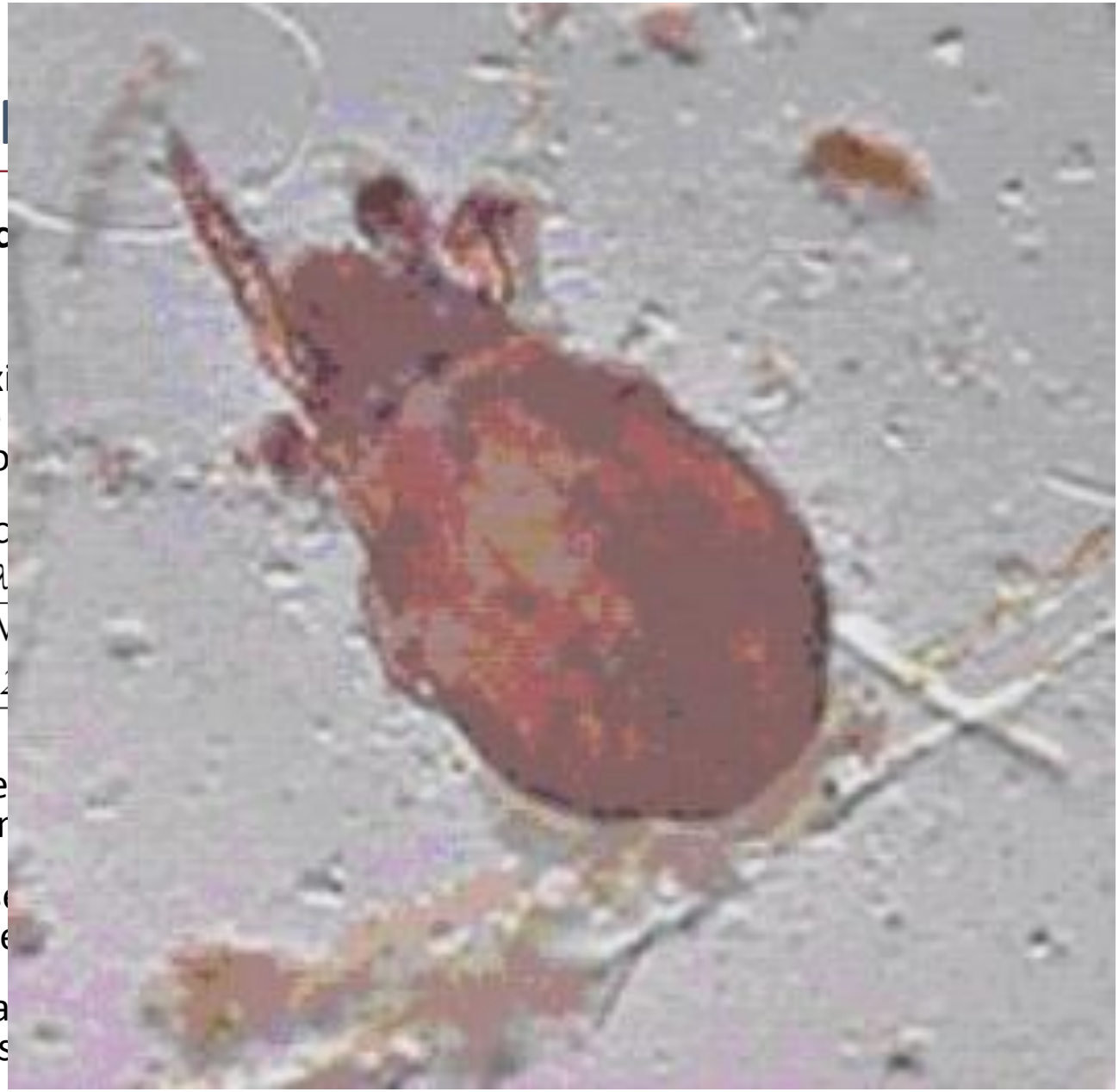


DEPTH OF FIELD

Depth of Field

The image is not only sharp at the optimum subject distance available for the lens, but from the lens and away from the lens within a range.

The range within the resolution of the microscope is perceived as one point.

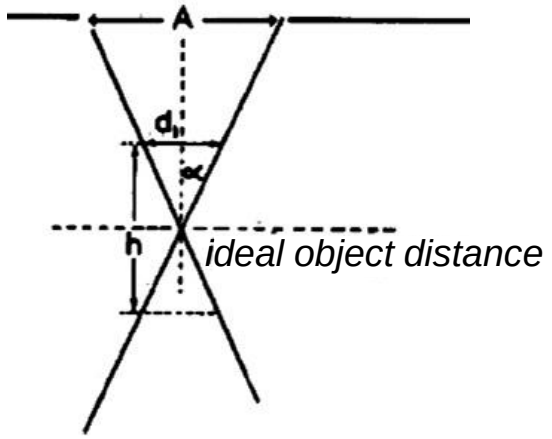
$$h = \frac{d}{tg\alpha} \qquad h = \mu \frac{\lambda}{n \sin\alpha \; tg\alpha} = \mu \frac{\lambda}{NA\, tg\alpha}$$

μ ~ *0.5*, for optical microscope α ~ *45°*, *tg*α ~ *1*

The depth of field matches to the maximum resolution.

In case of electron microscope $n = 1$, and α is usually very small, in this case $tan\alpha \sim sin\alpha$, so

$$h = \mu \frac{\lambda}{n \sin^2 \alpha} \approx \mu \frac{\lambda}{NA^2}$$



Possibilities to increase depth of field:
- wavelength increase
- reduction of the numerical aperture (with diaphragm).

THE ROLE OF ILLUMINATION

The intensity and direction of the illumination has a great impact in the case of optical and electron microscopy too.

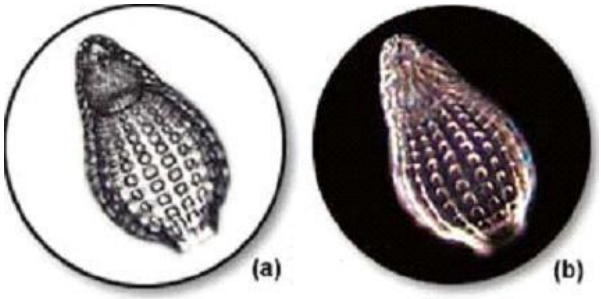
Bright Field Image

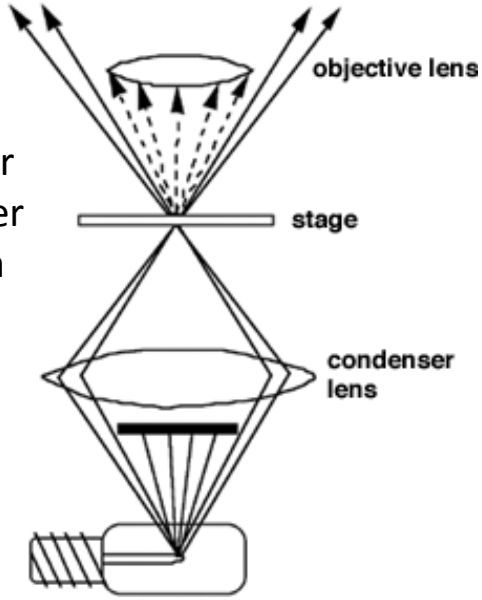
The illumination comes from under, perpendicular to the sample, parallel with the beam. Transmission mode,

The zeroth order diffraction (and also higher orders allowed by the aperture) reaches the objective.
Simple mode, but the contrast is small.

Dark Field Image

Tilted incident illumination from the side. The zeroth order diffraction does not reach the objective but multiple higher orders do which increases the contrast and the richness in details.





HISTORY – ELECTRON MICROSCOPES

- 1932-33: the first transmission electron microscope (TEM) (Knoll and Ruska). Ruska was awarded the Nobel Prize in 1986.
- 1935: Description of the concept of scanning (Knoll),
- 1939: The first analytical method in TEM, electron diffraction (Kossel and Möllenstedt)
- 1942: The first SEM, Zworykin
- 1965: The first commercially available scanning electron microscope (SEM, Cambridge Instruments)

Max Knoll
(17/7/1897 – 6/11/1969)

Ernst August Friedrich Ruska
(25/12/1906 – 27/5/1988)

HISTORY – ELECTRON MICROSCOPES

- 1944: Hillier and Baker records an electron-energy loss spectrum. This method is reinvented by Wittry, Ferrier and Cosslett, in 1969.
- 1951: Castaing builds the first micro-sensor, the device capable of the wavelength-dispersive electron-beam X-ray microanalysis.
- 1965: The SEM can be found in commercial use.
- Beginning of the 1970's: energy-dispersive microanalysis with a Si(Li) detector in SEM.
- 1973: J. A. Venables and C. J. Harland EBSD (Electron BackScatter Diffraction)
- 1989: Spectral imaging in electron-energy loss spectrometry (EELS) (Jeanguillaume and Colliex)
- 1990's: SDD (Silicon Drift Detector)

PROPERTIES OF THE ELECTRONS

Electron optics

Wavelength of a particle with **v** velocity and m mass:

$E = h \cdot \nu$
$E = m \cdot c^2$
$c = \lambda \cdot \nu$

$$\lambda = \frac{h}{m \cdot c} \xrightarrow{\text{de Broglie}} \lambda = \frac{h}{m \cdot v}$$

Kinetic energy of an electron accelerated by **U** voltage: $\frac{1}{2}\, \mathbf{m \cdot v^2 = e \cdot U}$

Wavelength of the electron: $$\lambda = \frac{h}{\sqrt{2 \cdot e \cdot m}} \cdot \frac{1}{\sqrt{U}}$$

Wavelength of an electron accelerated by 20 kV voltage:

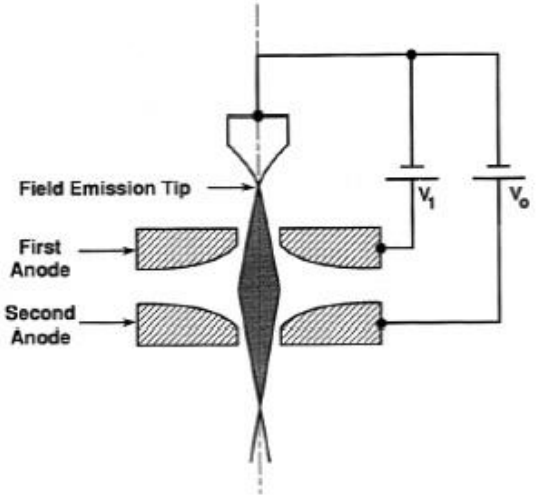
$$\lambda = \frac{6.64 \cdot 10^{-34}\,\mathrm{J \cdot s}}{\sqrt{2 \cdot 1.6 \cdot 10^{-19}\,\mathrm{C} \cdot 9.1 \cdot 10^{-31}\,\mathrm{kg}}} \cdot \frac{1}{\sqrt{20000\,\mathrm{V}}} = 8.7 \cdot 10^{-12}\,\mathrm{m} = 8.7 \cdot 10^{-3}\,\mathrm{nm}$$

ELECTRON SOURCES

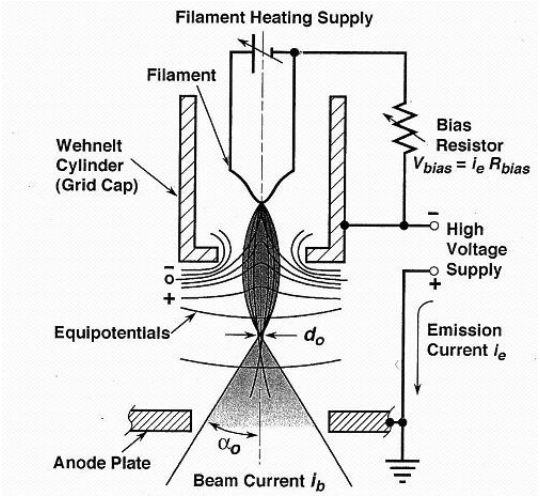
Electron gun

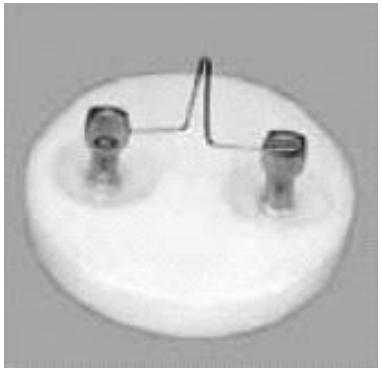
Thermal cathode: made from tungsten (*W*) or lantane-hexaboride (LaB_6).
Vacuum needed is: (10^{-3} - 10^{-5}) *Pa*.

Field emission source, usually with W tip..
The vacuum needed is much larger 10^{-8} *Pa*.

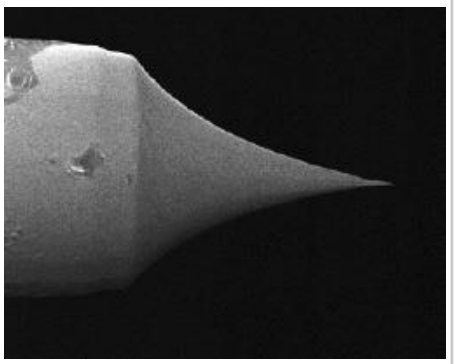


In novel TEM-s usually thermally assisted field emission source are used: **Schottky-source**.



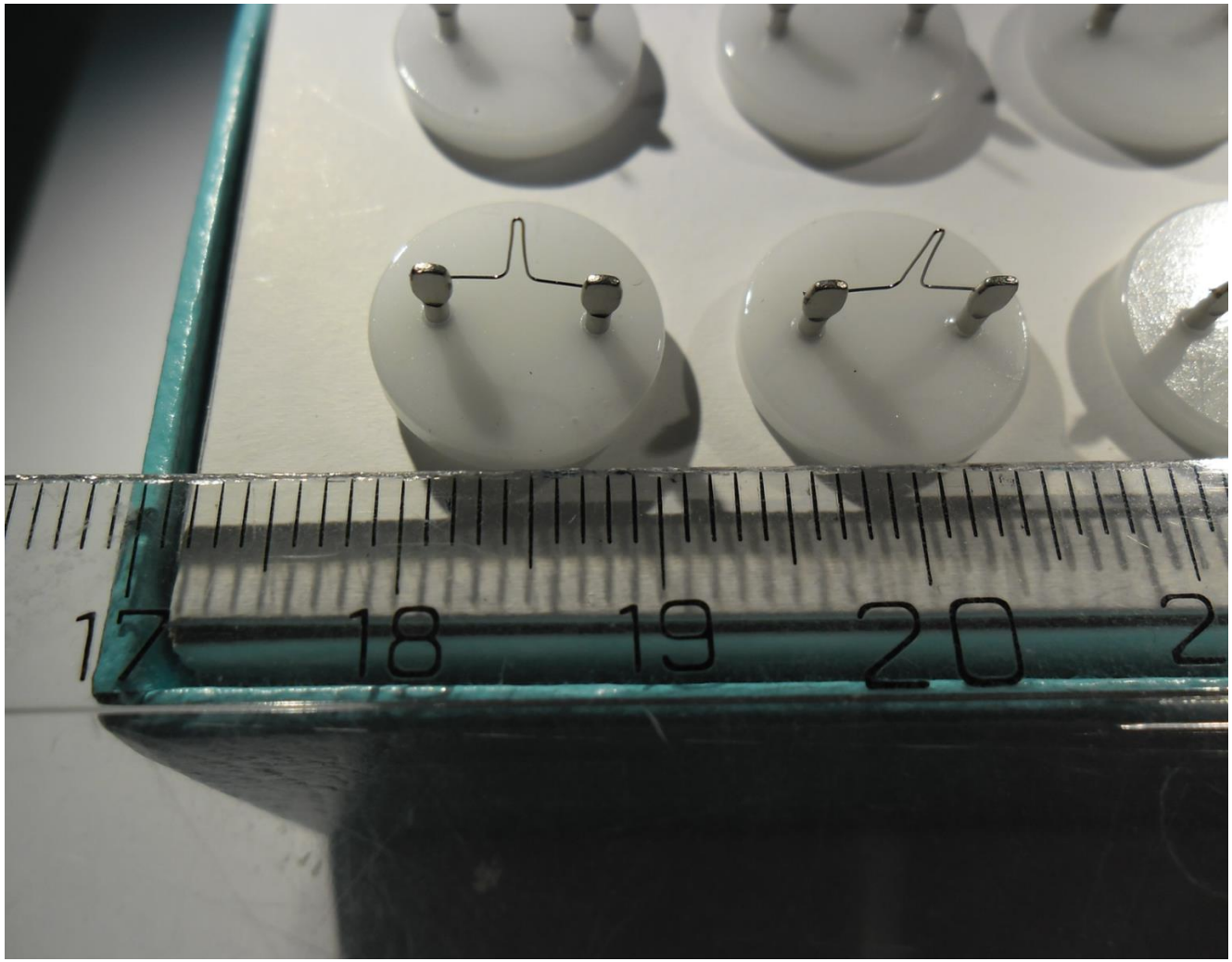


Thermal cathode



Field emission W cathode

THERMAL CATHODE (W)



ELECTRON OPTICS

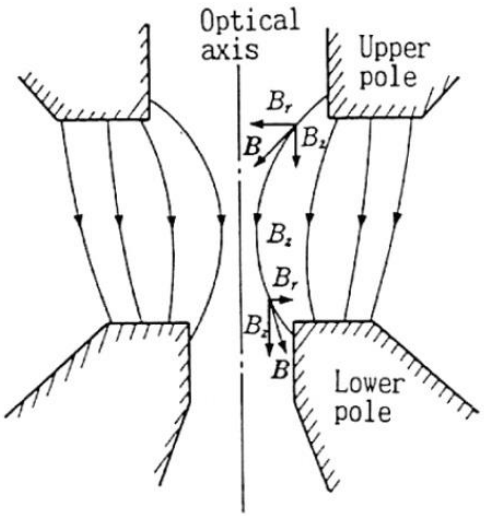
Electron lenses

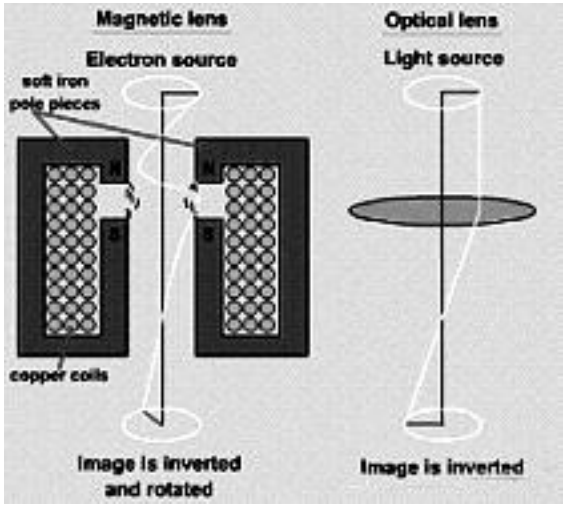
Magnetic lenses, based on the Lorentzian force.

The imaging of magnetic lenses is analogous with the imaging process of thin optical lenses.

Differences to optical lenses:

Due to the $\boldsymbol{F} = e\boldsymbol{v} \times \boldsymbol{B}$ Lorentzian-force, the electrons move spirally.
The focus distance can be adjusted by changing the current in the electromagnets.
The image of the optical lens is rotated by 180^{o}. In the case of magnetic lenses, it can be rotated by an arbitrary α degree depending on the parameters of the lenses.
The field of view is usually much smaller than in the case of optical lenses. ($u \sim 1^{o}$).
This means the numerical aperture $NA \sim 10^{-2}$, so the maximum resolution of the lenses is : $0{,}1\ nm$ in the case: $\lambda = 10^{-3}\ nm$.

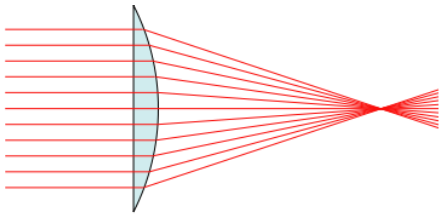




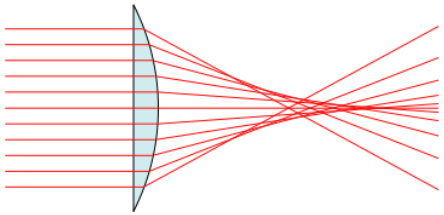
LENSE ERRORS

Spherical aberration

The incident beam diverges from the axis of the lens, so the focal point changes along the axis.



It can be corrected:
For example with two plano-convex lenses applied together with their planar side, or with properly chosen and assembled convex and concave lens.

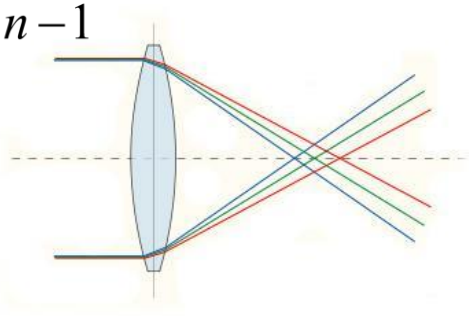


The error can be decreased by decreasing the aperture prior the lens.

Chromatic aberration

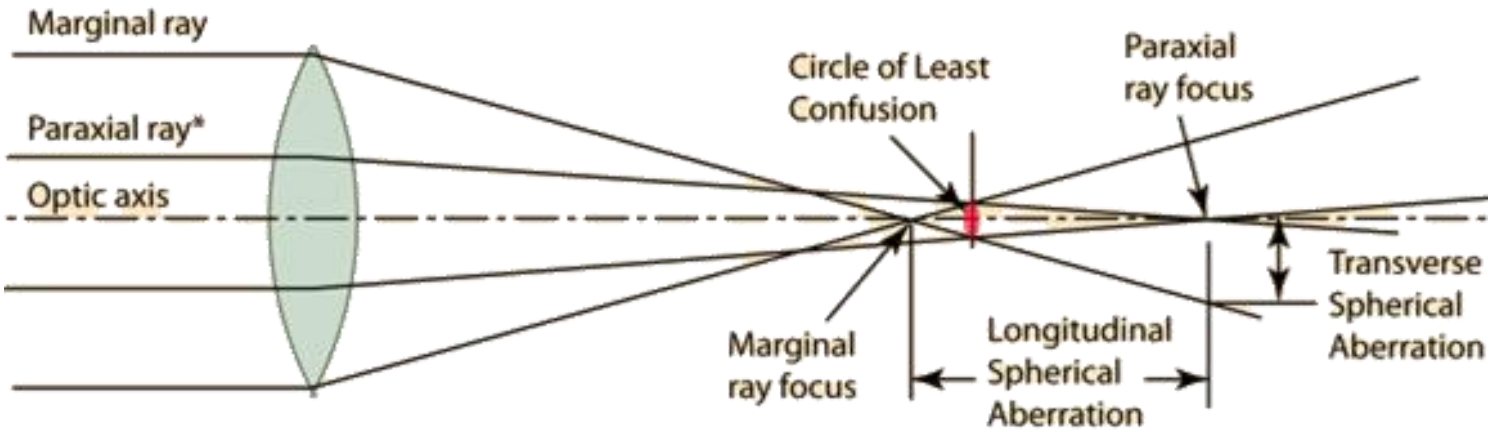
It is caused by the dispersion of the material of the lens.
The refraction coefficient is the largest for violet color, and it decreases systematically until the red color.
The image of the object, illuminated by white light, is red in the inside, violet outside.

$$f \sim \frac{1}{n-1}$$



With the combination of convex and concave lenses made of properly chosen material (crown or flint glass) the error can be partly corrected

SPHERICAL ABERRATION



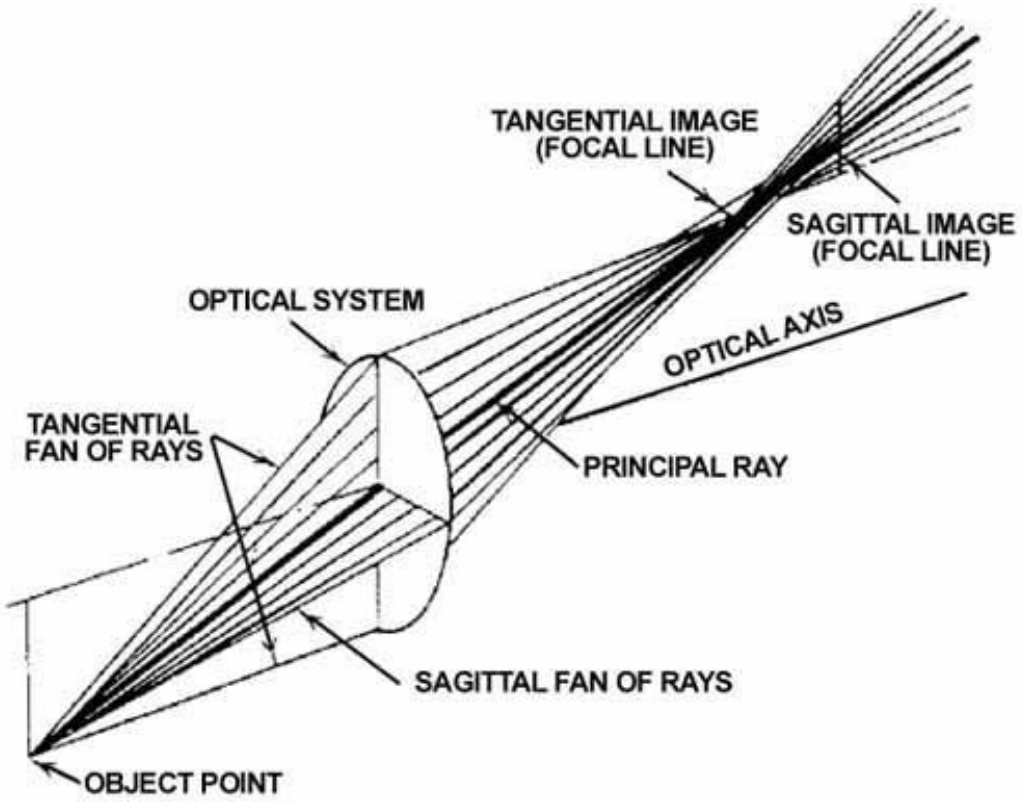
* Paraxial ray means a ray on the optic axis or very close to it, which the ray in the diagram is not. It is drawn further out to illustrate the idea of the circle of confusion.

LENSE ERRORS

Astigmatism

This phenomena occurs in the case of beams originating outside of the optical axis.

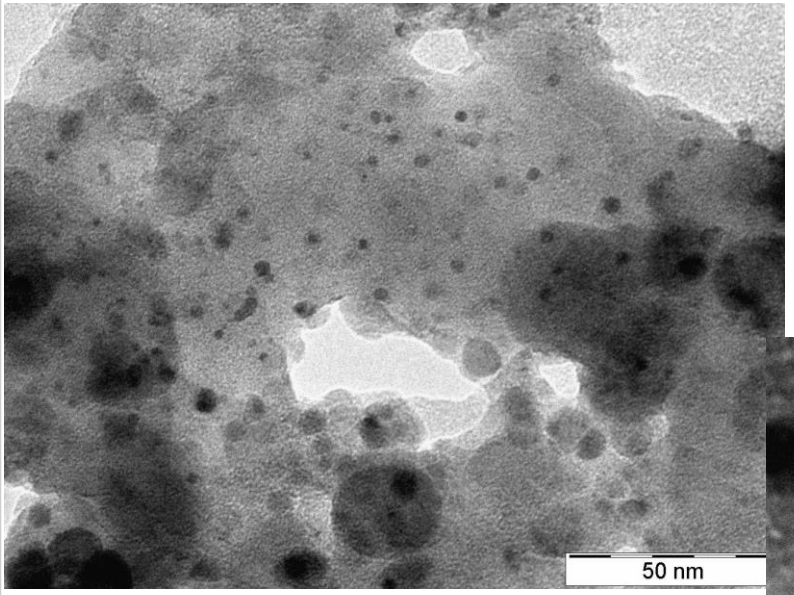
The beam crossing the lens horizontal axis (sagittal) and the beam perpendicular to it (tangential) do not have their focal points overlap.

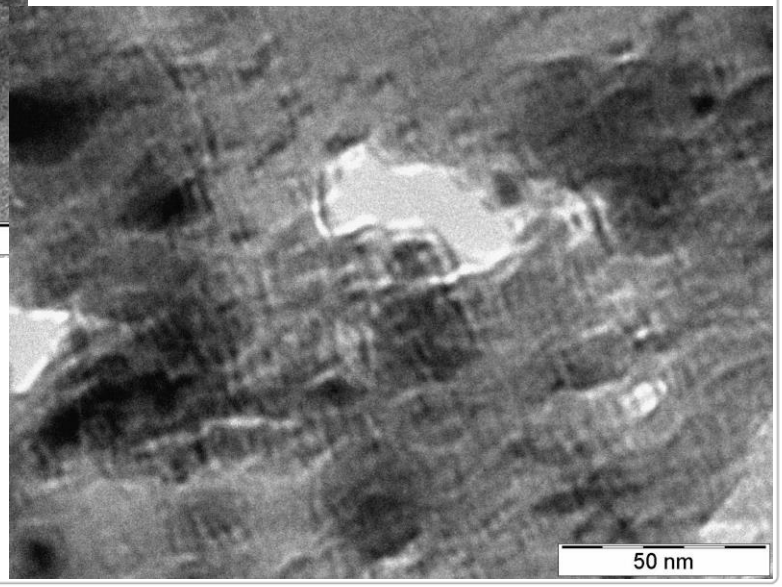


By reducing the diaphragm, we can reduce astigmatism.

ASTIGMATIS

OBSERVED ON TiB_2 SAMPLE (TEM)





ELECTRON OPTICS

Lens errors

Good resolution can be obtained by only using the best objective lenses. The optical lenses, similarly to the magnetic lenses, have lens errors.

In the case of electron lenses there are **spherical aberration**, **chromatic aberration** and the **astigmatism**.

The quality of the picture is usually determined by the properties of the objective,

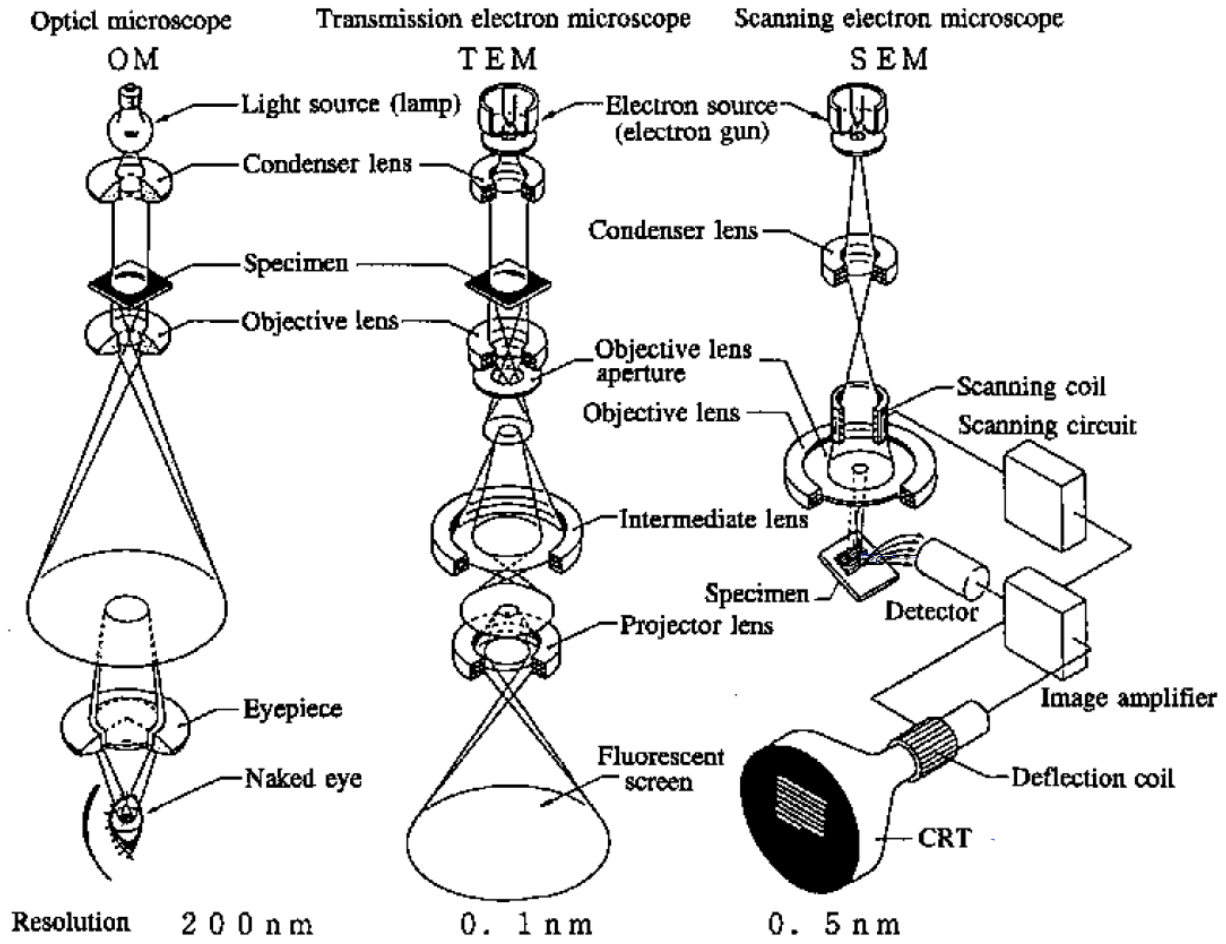
Spherical aberration

The spherical error can be evaluated by $C_s\alpha^3$, so it is proportional to the α subtense of the beam, participating in the imaging process, which can be adjusted by the optical aperture.
C_s is a constant depending on the lens.
In novel microscopes while decreasing the C_s we can improve the resolution.

In the case of an objective lens which is not corrected for the lens errors, we usually use only one diffraction beam in electron microscopy.

In High Resolution TEM (HRTEM) we need to use more sophisticated objective lenses.

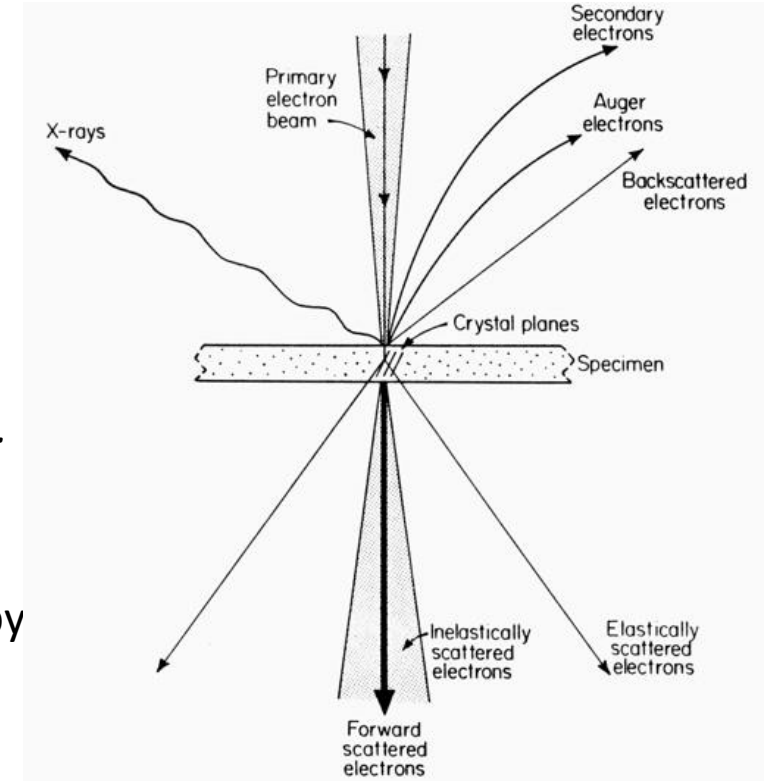
OPTICAL MICROSCOPE - TEM - SEM



ELECTRON-matter interaction

Interaction induced "products"

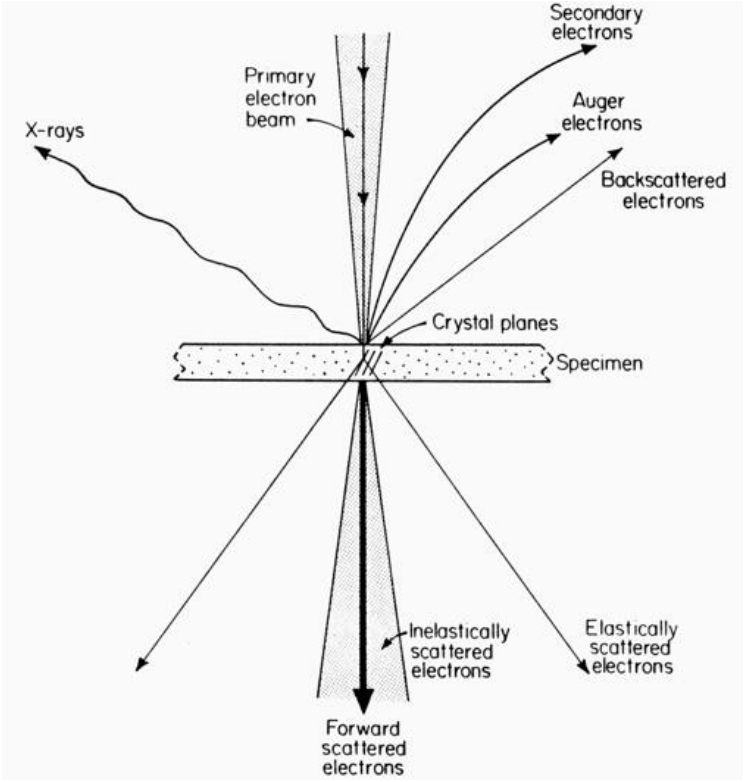
1. ***Forward-scattered electrons:*** no energy loss, no change of direction. Used for a bright-field image in transmission electron microscopy (TEM).
2. ***Inelastically scattered electrons:*** low energy loss, small angle scattering. Can be used for electron energy loss spectroscopy (EELS) and special imaging.
3. ***Elastically scattered electrons:*** there is no energy loss, the change of direction is in the order of degrees. In the case of crystalline material, the directions are determined by Bragg's law. It is used by TEM diffraction, TEM dark field image, and high resolution electron microscopy (HREM).



ELECTRON-matter interaction

Interaction induced "products"

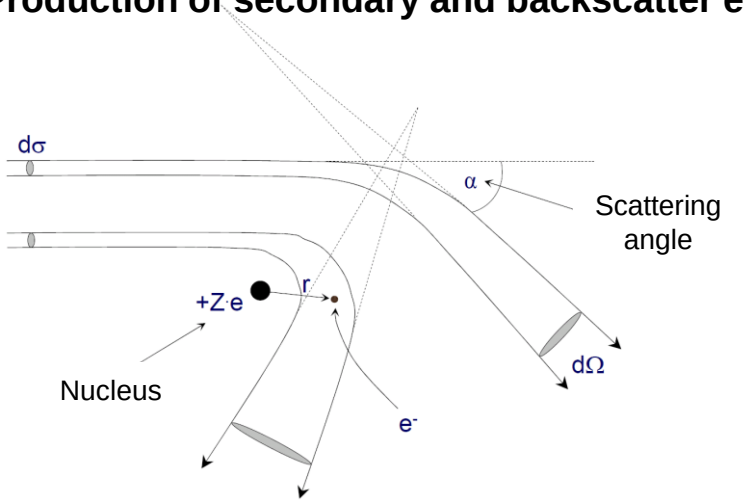
4. ***Secondary electrons:***
   Produced on the beam side of the sample.
   They are emerged from weakly bound electrons of the outer shell, which the beam shake out of their place. Used for collecting topographic (surface) information in scanning electron microscopy (SEM).

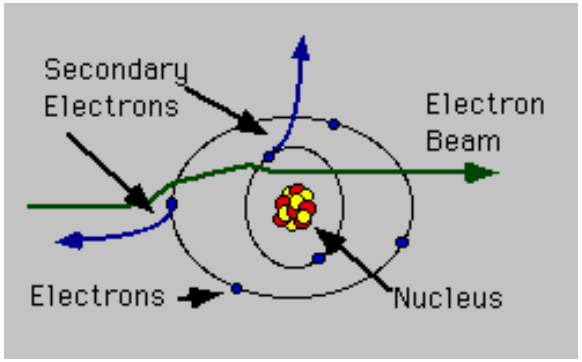


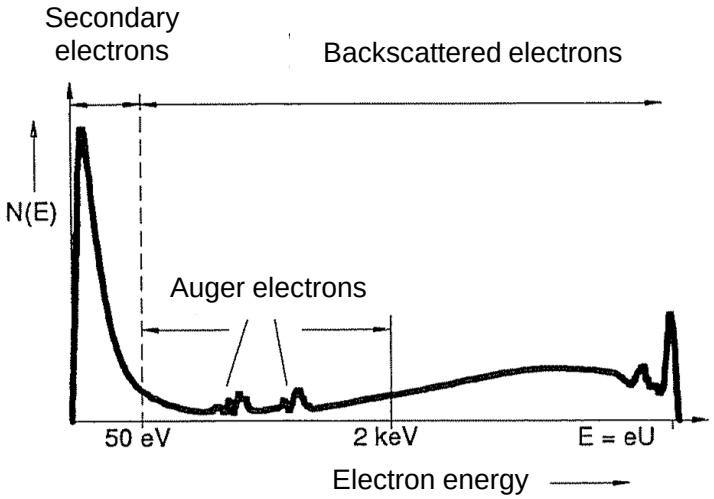
5. ***Backscatter electrons***. Originated from the exciting beam with high angular elastic or inelastic scattering. Used to use for imaging in SEM.

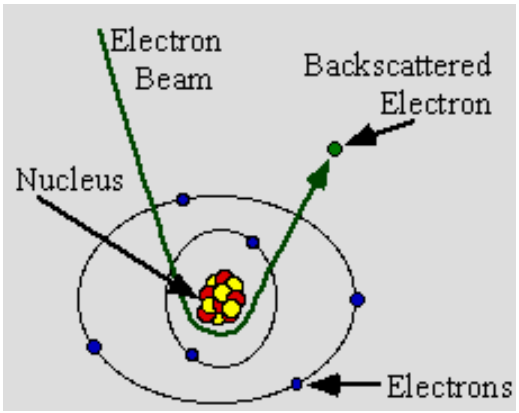
ELECTRON-matter interaction

Production of secondary and backscatter electrons





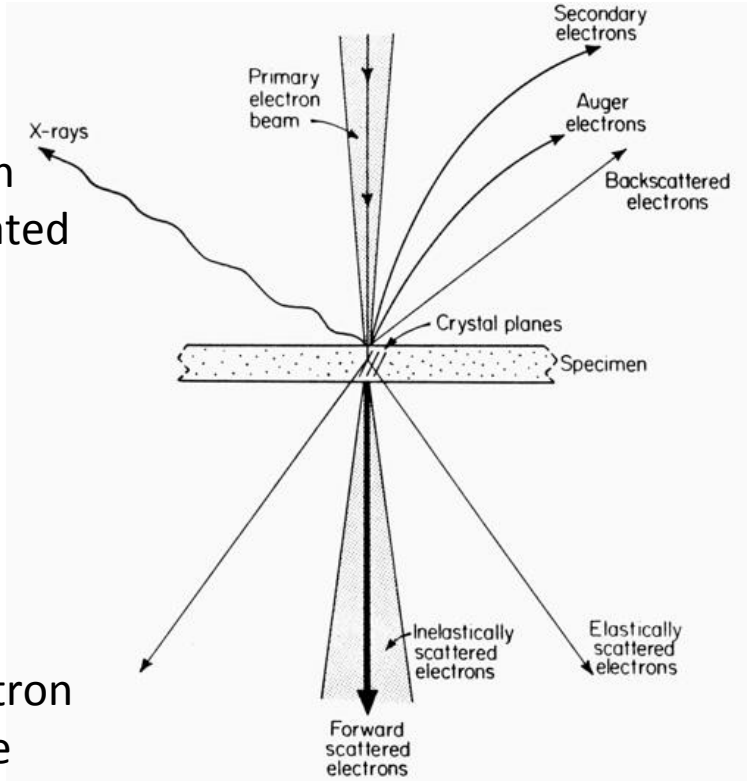




ELECTRON-matter interaction

Interaction induced "products"

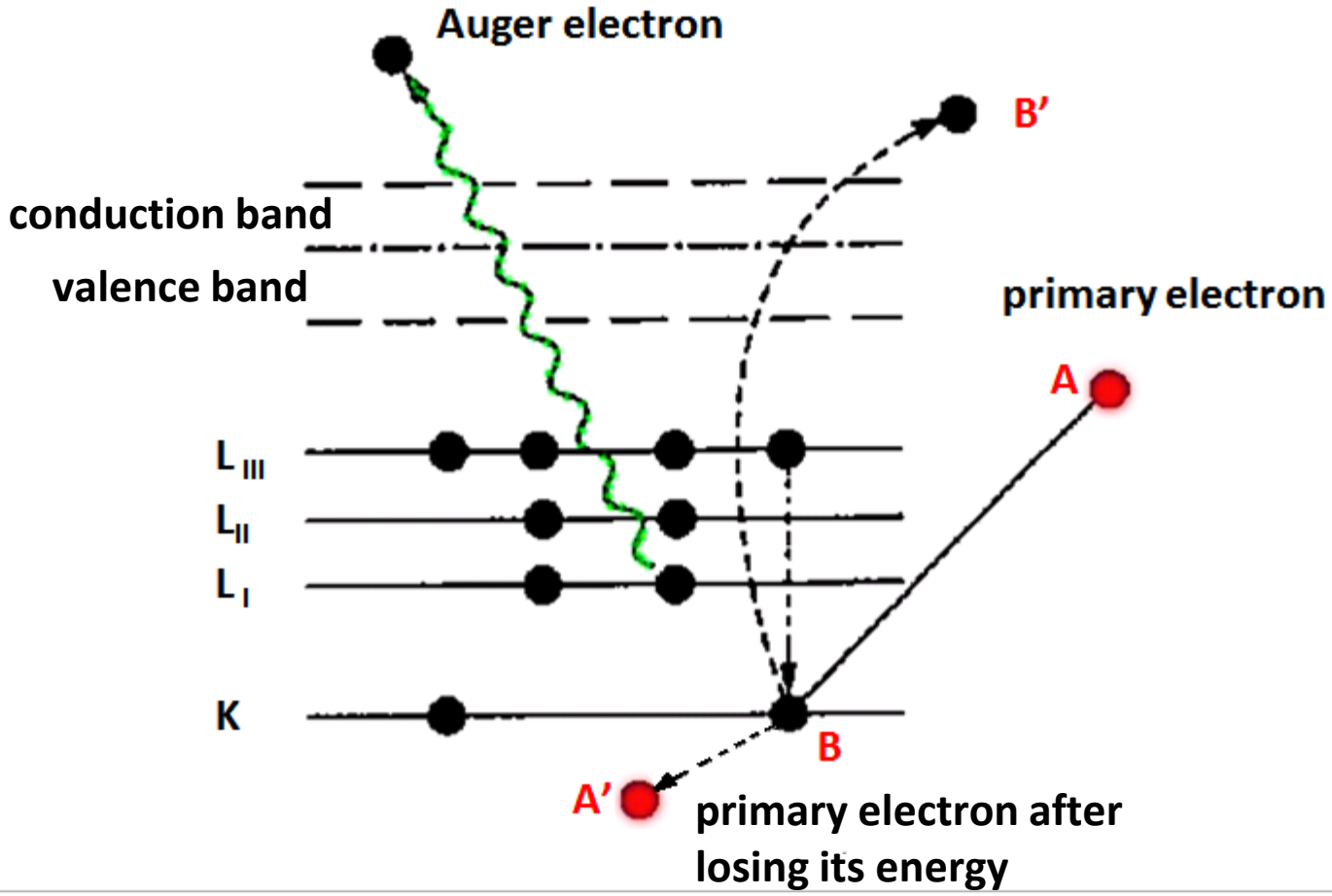
6. ***Characteristic X-rays :***
   As a result of the primary electron beam, an electron vacancy is created on the inner shell. During recombination an X-ray photon is emitted. It is the most commonly used signal in analytical electron microscopy (AEM). Used to determine chemical composition.



7. ***Auger electrons***:
   The electron beam ejects an electron from the inner shell of the sample atom; the electron hole is filled from a higher energy shell; the released energy is transferred to an electron at a higher energy level which leaves the atom. Used by Auger-electron spectroscopy to provide information about the chemical composition of the sample. It can be used primarily for surface analyzing.

ELECTRON-matter interaction

Product generation for analysis in e^- excitation process

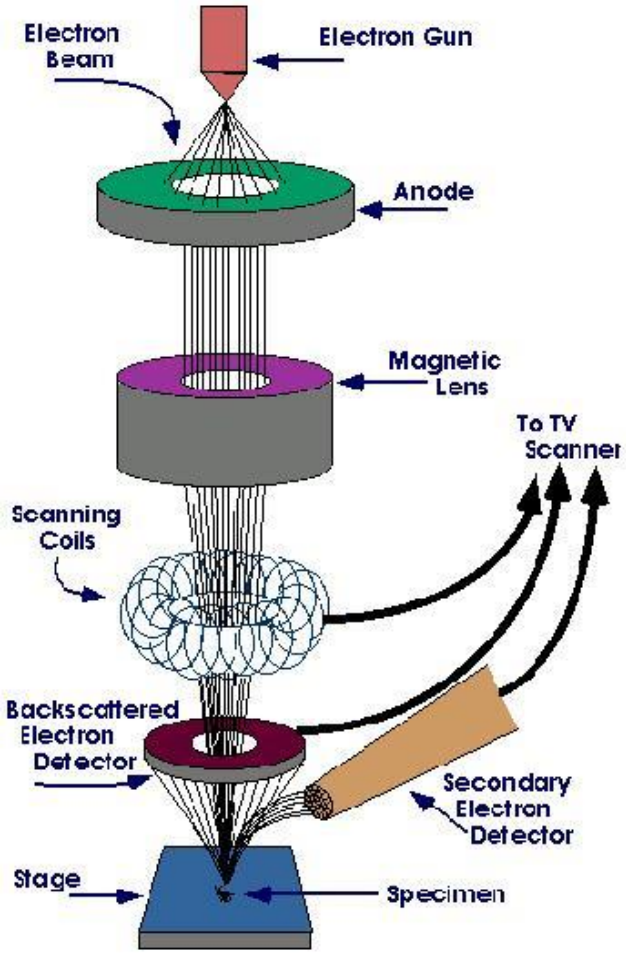


Electron Microscopy (SEM)

Scanning Electron Microscope (SEM)
(Pásztázó elektronmikroszkóp)

The first scanning electron microscope: Max Knoll, 1935.
The first commercial SEM appeared in the 1960s. It has spread since then. Tens of thousands of SEMs operate around the world. SEM creates an image of the object in a serial manner by point by point.

Source
The source is similar to that in the TEM, however, the beam exciting the sample is not parallel but focused.
The maximum energy of the electrons is usually $E_{max} = 30\ keV$, and the energy can be controlled in most microscopes.



Electron Microscopy (SEM)

Scanning Electron Microscope (SEM)
(Pásztázó elektronmikroszkóp)

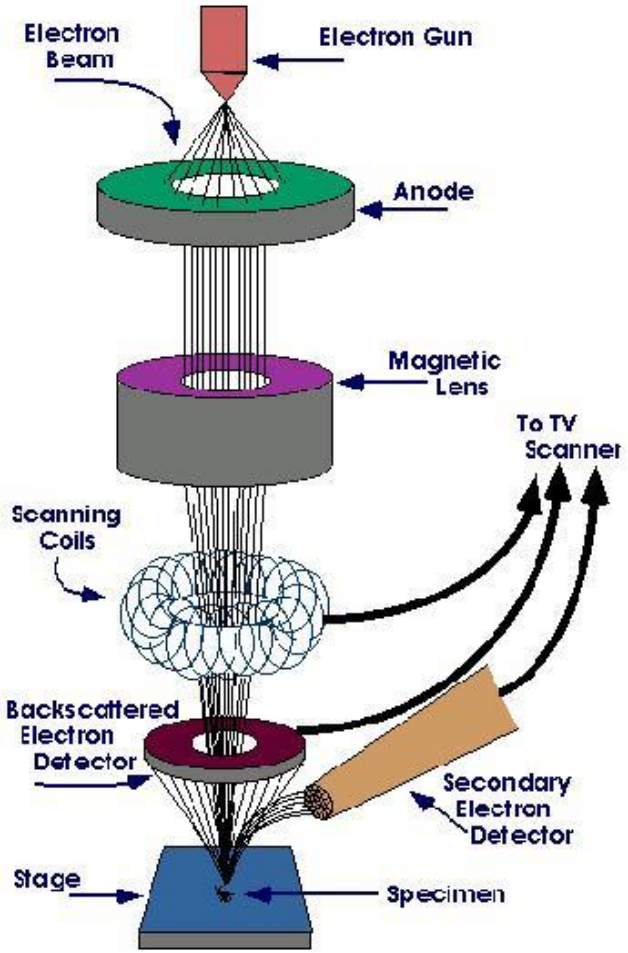
Electron beam
The beam diameter of the sample is *< 1 nm* for the best microscopes.
The beam scans the surface of the sample line by line.

Detected signals

In SEM,

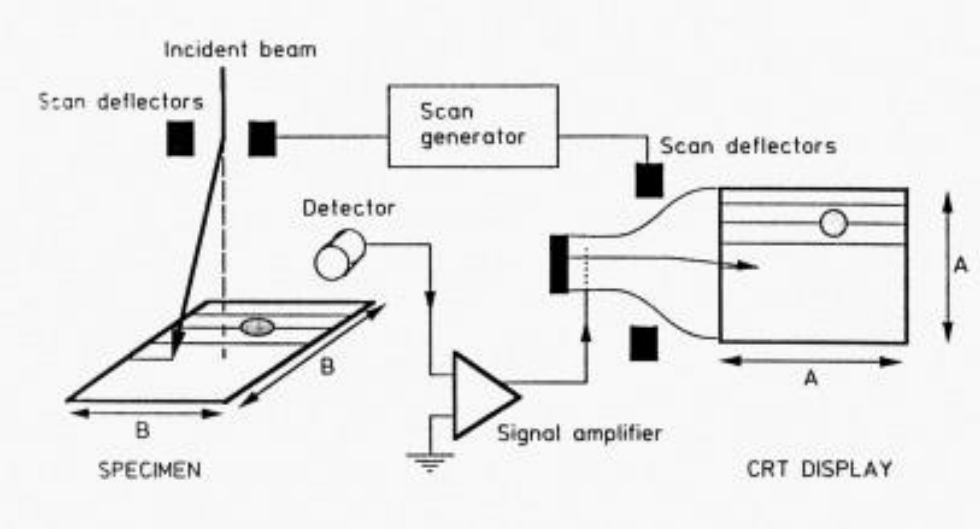
- **secondary electrons (SE),**
- **backscattered electron (BSE) and**
- **X-ray photons**

are used to generate the image.



Electron Microscopy (SEM)

Principle of imaging:



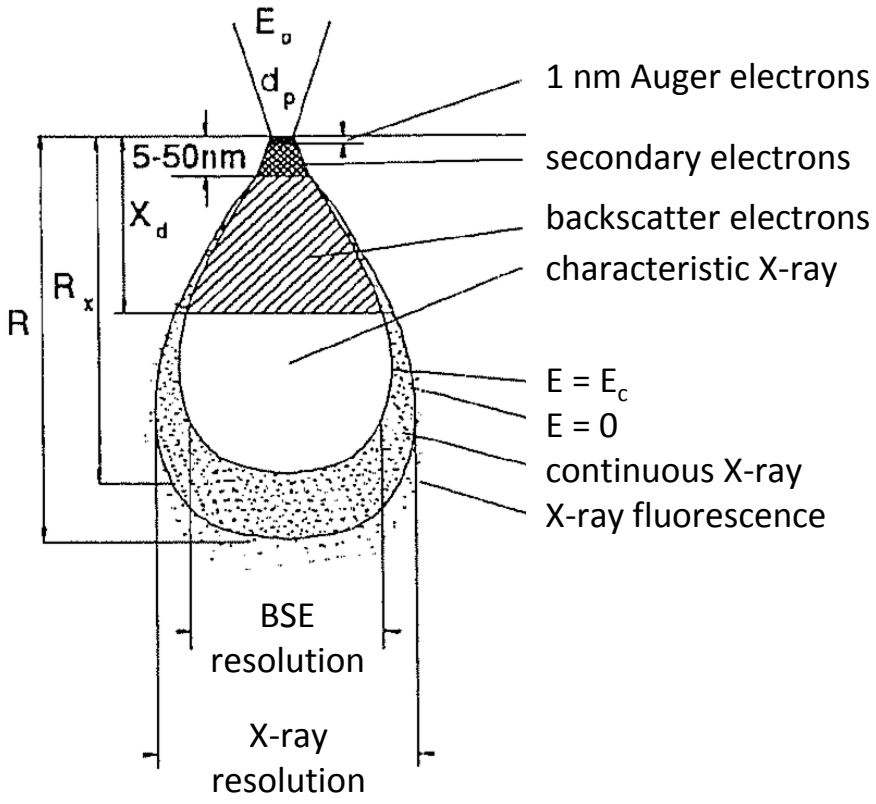
The electron beam scanning the surface of the sample is controlled by the scanning generator.
The same generator controls the activation of points on the screen point by point.
The number of electrons or X-ray photons generated by the e- beam is detected by special detectors.
The signal from the detectors modulates the intensity of the respective points on the screen.
If the sample surface emission changes, this change is displayed on the screen.

Electron Microscopy (SEM)

Principle of imaging:

The “products” ejected from the surface of the sample have different energies and therefore they come from different depths and different volumes.

In addition to the diameter of the electron beam, this is what determines the resolution.

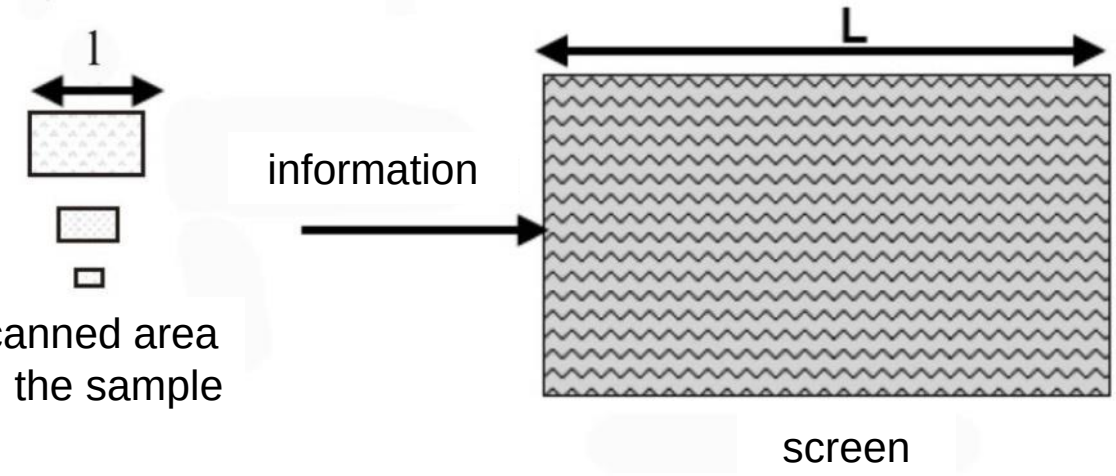


Electron Microscopy (SEM)

Magnification

The magnification of the SEM is essentially determined by geometric conditions.

$$N = \frac{L}{l}$$



Maximum (effective) magnification:

$$N_{max} = \frac{screen\ size\ in\ pixel}{raster\ size\ on\ the\ specimen} = \frac{H}{n\ d}$$

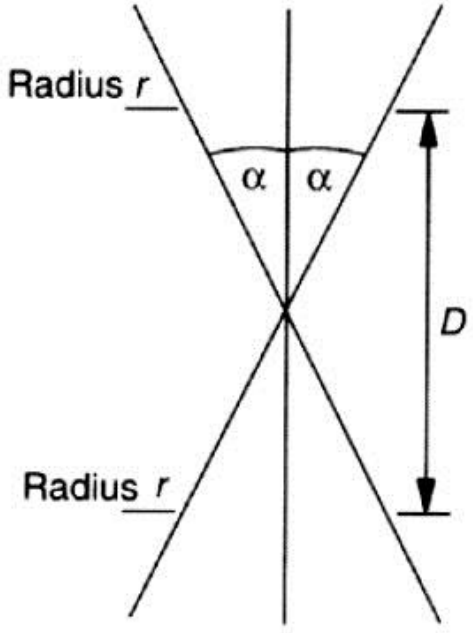
For example, H = 40 cm, n = 10^3 and d = 1 nm gives N = 4 · 10^5.

Electron Microscopy (SEM)

Depth of field (Mélységélesség)**:**

$$D = \frac{2r}{\alpha}$$

The 2r diameter beam should be a separate point in the image as long as the magnified image falls within 1 screen pixel.



$$2rN = K_p$$

K_p display pixel size

$$D = \frac{K_p}{N\alpha}$$

Can be see that the lower the magnification, the greater the depth of field.
For example: $K_p = 0{,}1\ mm$, $N = 10^3$, $\alpha = 10^{-2}$ gives $D = 0{,}01\ mm = 10\ \mu m$.
For $N = 10^5$ the depth of field: $D = 10^{-4}\ mm = 0{,}1\ \mu m$.

Electron Microscopy (SEM)

- Thick samples can also be measured.
- It requires less preparation than TEM samples.
- Contamination should be removed from the surface before testing
- During SEM examination, charge is transferred to the sample surface and must be removed.

For **conductive samples**, the charge is removed through the grounded sample holder.

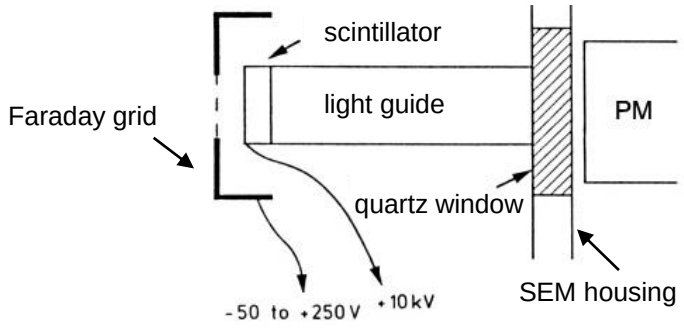
For **insulating samples** there are several methods to prevent charge build-up.

1. A common solution is to coat the sample surface with a thin layer of *Au* or *C*.
   The advantage of carbon is that the *C* atoms contain fewer electrons, which makes X-ray analysis advantage in X-ray because it results in a smaller X-ray background.
2. Energy filtering of the signal to the detector
3. Low vacuum solution

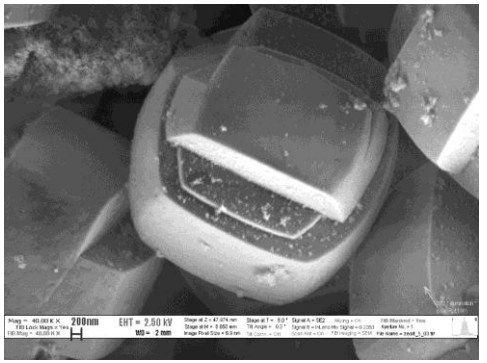
Electron Microscopy (SEM)

Features of the secondary electron image

- In most cases we use this.
- These electrons
  - had a broad energy distribution but low energy *(E < 50 eV)*.
  - only reach the surface from a small depth *(~ 0.1 nm)*.
  - relatively easy to collect.



Everhart-Thornley detector



zeolit crystal $N = 4 \cdot 10^4$

- The secondary electron image mainly carries information about the thin layer near the surface and is mainly used to study the surface morphology.
- At low magnification a high depth of field can be achieved; 3D quality images can be obtained.

Electron Microscopy (SEM)

Features of the backscattered electron image

- backscattered electrons
  - have a relatively high energy (*E ~ 10-30 keV*),
  - more difficult to collect than low-energy secondary electrons,
  - detected by a semiconductor detector placed in a circular pattern above the sample, or by a simple conductive annular ring plate.
- the maximum resolution is usually lower than for secondary electrons.
  - the excited volume is larger than the diameter of the beam at the sample surface
- the image shows a so-called Z-contrast.
  - the yield depends on the number of electrons of the scattering atom.

The image shows SE (below) and BSE (above) images of an Al sample with Zr precipitates from the same region.

The SE image shows the surface relief, while the BSE image with Z-contrast shows the Zr precipitates clearly on the top.